

Via this reaction, we surprisingly directly obtained not only **1** but, in addition, two isomers, which we assign^[8] to the unexpectedly stable *syn,syn,anti*- and *syn,anti,anti*-conformations **9** and **10**^[7] (Fig. 1) on the basis of their ¹H-NMR spectra and their thermal rearrangement to give **1**.

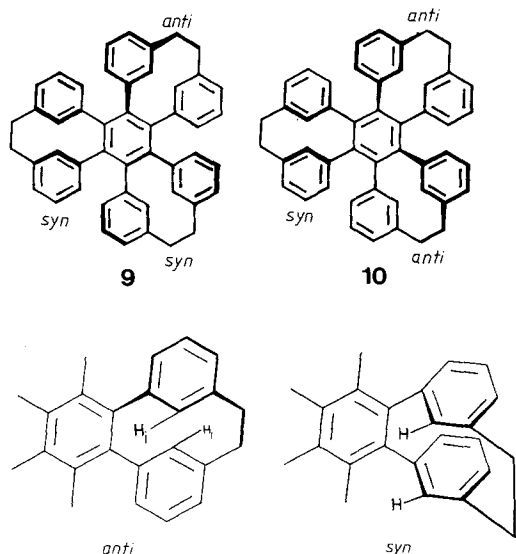


Fig. 1. *anti*- and *syn*-Arrangements (selected) in **1**, **9**, and **10**.

Upon heating of the products of the phenyllithium cyclization to 350°C, a *syn*→*anti* rearrangement takes place, which is at first apparent by change in the crystal structure under the hot-stage microscope, but also in the completely changed ¹H-NMR spectrum (Fig. 2). Whereas the *syn* conformers **9** and **10** exhibit arene signals at $\delta = 5.15$, 5.22, and 5.45 as well as CH₂ signals centered at $\delta = 2.1$ and 3.2, the ¹H-NMR spectrum of **1** proves its structure on the basis of the strong high-field shifts of the inner protons [$\delta(H_i) = 5.4$]. The inner protons of the comparison compound **2** absorb at the same field strength ($\delta = 5.44$).

Racemic **1** (all-*anti*) is almost colorless; above 380°C, it turns brown^[9]. A base-line separation of the racemic mixture of **1** was achieved by HPLC on (+)-poly(triphenylmethylmethacrylate) [(+)-PTrMA]^[10]. As expected, the optical rotations are high: $M_{436}^{22} = +5235$ ^[9].

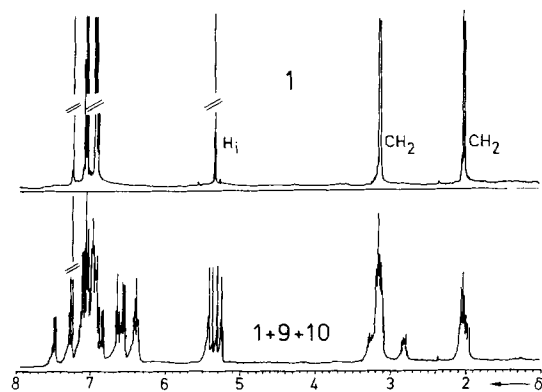


Fig. 2. ¹H-NMR spectra of the synthetically obtained mixture of **9**, **10**, and **1** (below) and of pure **1** (above): 400 MHz, in CDCl₃.

As expected, the optical stability of the new molecular propeller **1**, which is important for practical applications^[11], is considerable; it is even higher than that of the helixenes. **1** even sustains heating at 310°C for several minutes—conditions that lead to the racemization of the helixenes as well as of **2**. This is plausible since the inversion of a phenylene group in the *anti*-position is coupled with that of each of the other five, in contrast to the independent ring inversion in **2**.

By analogous synthetic strategy, other helices, with high optical rotation and stability, might be accessible^[12]. The dehydrogenation product of **1**, a diphenanthrovalene, is also of interest due to its polycyclic aromatic structure.

Received: December 5, 1984 [Z 1099 IE]
German version: *Angew. Chem.* 97 (1985) 227

CAS Registry numbers:

(±)-**1**, 95216-91-4; (+)-**1**, 95340-76-4; (–)-**1**, 95340-77-5; **3**, 35286-92-1; **4**, 74844-03-4; **5**, 95216-92-5; **6**, 95216-93-6; **7**, 95216-94-7; **8**, 95216-95-8; (±)-**9**, 95340-78-6; (±)-**10**, 95342-08-8.

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- [5] This may be compared with the *achiral para*-bridged "trifoliaphane": M. Psioz, H. Hopf, *Angew. Chem.* 94 (1982) 639; *Angew. Chem. Int. Ed. Engl.* 21 (1982) 623.
- [6] Name according to IUPAC nomenclature: Decacyclo[37.3.1.1^{4,8}.1^{11,15}.1^{18,22}.1^{25,29}.1^{32,36}.0^{2,31}.0^{3,16}.0^{17,30}]octatetracontal(42),2,4(48),5,7,11(47),12,14,16,18(46),19,21,25(45),26,28,30,32(44),33,35,39(43),40-henicosane.
- [7] M.p. [°C]: **5** 206; **6** 64; **7** liquid, R_f value = 0.39 (CHCl₃/acetone 9 : 1); **8** 266; **9** rearrangement to **1** above ca. 300; **10** rearrangement to **1** above ca. 300.
- [8] Examination of molecular models plausibly explains the lack of formation of the all-*syn* conformer, in which a sterically less-favorable arrangement of the six peripheral benzene rings should be present.
- [9] Elemental analyses and spectra of the new compounds are in agreement with the structures given. The weighing of small amounts of **1** poses some difficulties owing to its strong electrical charge. The optical rotation of the (–)-enantiomer is of the same order of magnitude as that of the (+)-enantiomer.
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- [11] Cf. G. Solladié, R. G. Zimmermann, *Angew. Chem.* 96 (1984) 335; *Angew. Chem. Int. Ed. Engl.* 23 (1984) 348.
- [12] Cf. a) F. Vögtle, M. Palmer, E. Fritz, K. Meurer, U. Lehmann, A. Mannschreck, F. Kastner, U. Huber-Patz, H. Puff, E. Friedrichs, *Chem. Ber.* 116 (1983) 3112; b) M. Witte, F. Vögtle, *ibid.* 115 (1982) 1363.

"Stereochemical Activity" of a Lone Pair of Electrons on Low Valent Elements of the 4th Main Group: (GeN^rBu)₄·2 AlCl₃ and (SnN^rBu)₄·2 AlCl₃**

By Michael Veith* and Walter Frank

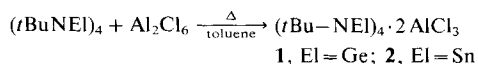
Dedicated to Professor Gerhard Fritz on the occasion of his 65th birthday

The "stereochemical activity" of a lone pair of electrons on heavy main group elements has often been discussed

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[**] Cyclic Diazastannylenes, Part 21. This work was supported by the Fonds der Chemischen Industrie.—Part 20: M. Veith, W. Frank, *Angew. Chem.* 96 (1984) 163; *Angew. Chem. Int. Ed. Engl.* 23 (1984) 158.

with resort to bond theory and structural and chemical aspects for evidence of the existence or non-existence of such an activity. In the case of molecular compounds of divalent elements of the fourth main group (especially of Ge^{II} and Sn^{II}), primarily the existence of transition-metal complexes of the type X_nM—Ely₂^[2] or [X_nM—Ely₃]^{⊖[2]} (El=Ge, Sn) has been taken as supporting evidence for these elements being able to function as bases by virtue of the lone pair of electrons; however, the particular electronic structure of the transition metal was ignored (back-bonding etc., cf. also carbene complexes^[3]). Even though a whole series of acid-base adducts such as (Cp)₂Sn—AlX₃^[2] (Cp = cyclopentadienyl, X = halogen) and X₂Sn—BF₃^[2] have been reported, neither the exact structures are known, nor is the formulation of the compounds as adducts confirmed. According to most recent structure investigations even the species (η⁵-C₅H₅)₂Sn—BF₃ designated as adduct must be described as [(BF₄)[⊖]]{(μ-η⁵-C₅H₅)₂Sn(μ-η⁵-C₅H₅)[⊖]·thf}_n^[4]. By reaction of the cubane-like compounds (GeNtBu)₄^[5] and (SnNtBu)₄^[5] with aluminum trichloride we have now succeeded in preparing adducts which contain Ge—Al and Sn—Al bonds, respectively. By varying the molar ratio of the reaction partners, we have tried to prepare the adducts (tBuNEl)₄·(AlCl₃)_x with x = 1—4; however, on crystallization only those adducts with x = 2 could be isolated.



The ¹H-NMR spectra of the reaction solutions surprisingly contain (see molecular structure in Fig. 1) only one singlet, whose chemical shift depends upon the ratio of the reaction partners (when x = 2, 1: δ = 1.30 (s); 2: δ = 1.32 (s), 60 MHz, 28°C, toluene)^[6]. This finding could be explained in terms of the presence of various adducts and a rapid exchange of the AlCl₃ groups in solution. An X-ray structure analysis on single crystals of 2 confirmed the adduct structure. 1 and 2 are relatively unstable; they decompose into the starting components, slowly in solution and rapidly under reduced pressure (in the mass spectrometer).

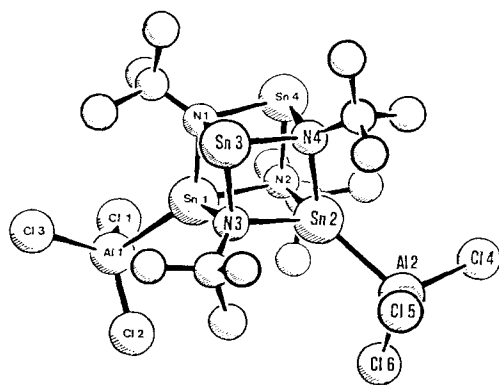


Fig. 1. Structure of 2 in the crystal. The unnamed atoms are carbon atoms; the hydrogen atoms of the methyl groups are not shown. The Sn₄N₄ skeleton is retained on adduct formation, the point symmetry of 2 is almost C_{2v} (mm2). Cell dimensions: a = 1032.5(5), b = 2311.2(9), c = 1981.4(8) pm, β = 124.3(1)°. Space group: P2₁/c; Z = 4. Four-circle diffractometer, R = 0.074 with a reflection-parameter ratio of 14.07 : 1. Some selected (averaged) bond lengths: Sn—Al 278(1), Al—Cl 212.4(8), Sn—N 219(2), N—C 150(1) pm. Further details of the crystal structure investigation are available on request from the Fachinformationszentrum Energie Physik Mathematik, D-7514 Eggenstein-Leopoldshafen 2, on quoting the depository number CSD 51 183, the names of the authors, and the full citation of the journal.

The structure analysis of 2 (Fig. 1) proves for the first time that low-valency elements such as Sn^{II} can function as donors in Lewis acid-base adducts. The Sn—Al bond length corresponds exactly to that expected from the atomic radii^[7]; the aluminum atoms coordinate in a distorted tetrahedral fashion, with the Cl—Al—Cl angle of 113.9° (mean) lying in the range typical for AlCl₃ adducts^[8]. On comparing the structure of 2 with the structure of the uncoordinated (SnNtBu)₄^[9] the following differences emerge: a) the distance between the fourfold coordinated tin atoms in 2 is reduced (Sn1···Sn2 = 323.6(2) pm, in (SnNtBu)₄: 333 pm^[9]), while the other intramolecular distances all remain, within the standard deviations, the same. b) As a direct consequence of this closing-up, the N—Sn—N angles in the four membered ring N2—Sn1—N3—Sn2 (84° in 2 compared to 80° in (SnNtBu)₄) are widened and the Sn—N—Sn angles compressed. A very superficial interpretation of this effect could lead to the conclusion that the distance between the respective tin atoms becomes smaller by withdrawal of the electron density of the lone electron pairs. The adducts 1 and 2 support the hypothesis that the (tBuNEl)₄ molecules (El = Ge, Sn) may better be described as cage molecules with oriented bonding^[9]. But it is still unclear why only the adducts with two AlCl₃ moieties crystallize and not also those with another Al : Sn ratio.

Experimental:

Newly sublimed aluminum trichloride (0.152 g, 1.14 mmol) was treated with a solution of (tBuNGe)₄^[5] or (tBuNSn)₄^[5] (0.58 mmol) in toluene (30 mL) in the strict absence of moisture. On heating the mixture to boiling the AlCl₃ dissolved. The resulting solution was concentrated by evaporation and allowed to stand. After a few hours, rhombus-shaped crystals separated out. Yields: 1, 0.36 g (75.6%); 2, 0.38 g (65%). The crystals gave correct elemental analyses.

Received: November 13, 1984 [Z 1067 1E]
German version: *Angew. Chem.* 97 (1985) 213

CAS Registry numbers:

1, 95156-17-5; 2, 95156-18-6; (t-BuNGe)₄, 84805-53-8; (t-BuNSn)₄, 95156-19-7; Al, 7429-90-5; Sn, 7440-31-5.

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Mechanism of Purpurogallin Formation: An Adduct from 3-Hydroxy-*o*-benzoquinone and 4,5-Dimethyl-*o*-benzoquinone

By Walter Dürckheimer* and Erich F. Paulus

Dedicated to Professor Rolf Sammet on the occasion of his 65th birthday

Purpurogallin 1, found in nature as a glycoside, is formed upon oxidation of pyrogallol in water. The mechanism of this reaction is still largely speculative. Salfeld^[1] and Horner et al.^[2] postulated an intermediate 3 formed

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